

Ionic and Radical Addition of Methyl Hypochlorite to Dienes

Gene E. Heasley,* Vicki M. McCully, and Ralph T. Wiegman

Department of Chemistry, Bethany Nazarene College, Bethany, Oklahoma 73008

Victor L. Heasley and Randy A. Skidgel

Department of Chemistry, Point Loma College, San Diego, California 92106

Received September 4, 1975

The products (chloro ethers and dichlorides) obtained from the reaction of butadiene (1), isoprene (2), and the 1,3-pentadienes, *cis*- (3a) and *trans*- (3b), with chlorine in methanol, methyl hypochlorite in methanol, and methyl hypochlorite under radical conditions are reported. Analysis of product compositions suggests that chlorine and methyl hypochlorite react via essentially identical carbonium ion intermediates in methanol and that in the absence of methanol, methyl hypochlorite reacts via a radical mechanism only. Ionic electrophilic attack by chlorine occurs only at the 1,2 bond in 2 and predominantly at the 1,2 bond in 3a,b, suggesting that the transition states for the reactions are carbonium ion-like.

Alkyl hypochlorites (ROCl) have been utilized extensively¹ in radical reactions but their potential for ionic reactions has received limited attention. Reports in the literature² and observations of our own indicated that polar electrophilic additions of hypochlorites to alkenes apparently occurred in protic solvents (alcohols, carboxylic acids, and water). We decided to investigate the reaction of methyl hypochlorite with the conjugated dienes, butadiene (1), isoprene (2), *cis*-1,3-pentadiene (3a), and *trans*-1,3-pentadiene (3b) in methanol. Since earlier studies had made no clear distinction between ionic additions and possible radical reactions, we needed to clarify the conditions necessary for each mechanism. Our principal interest in studying the addition of methyl hypochlorite to dienes centered around the hope that this unsymmetrical electrophile would furnish insights into diene addition mechanisms which could not be obtained from symmetrical electrophiles such as bromine and chlorine. With methyl hypochlorite, the site of initial electrophilic attack on the diene is marked in the product with chlorine, permitting an assessment of the relative reactivities of the 1,2 vs. the 3,4 double bonds in 2, 3a, and 3b. The site of nucleophilic attack in the addition is confirmed by the position of the methoxyl group, which should afford an insight into the nature of the bonding in the intermediates.

Results and Discussion

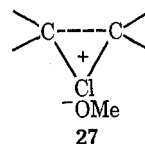
Table I shows the products which were obtained from the four dienes and the three reagents, chlorine (in methanol), methyl hypochlorite (in methanol), and methyl hypochlorite (radical addition).

Radical addition was accomplished simply by addition of the hypochlorite to the neat diene (or in solution at high diene concentration) where a molecule-induced homolysis occurred.

In dilute solution in methylene chloride (0.02 mol fraction in diene) the radical addition of methyl hypochlorite was greatly retarded and no reaction occurred in the presence of oxygen. In dilute methanol solution (0.02 mol fraction in diene) methyl hypochlorite reacted readily at 0°C, affording high yields of chloro ethers. The 1,2-chloro ethers exhibit the structure expected for Markownikoff addition of a positive halogen compound. Chlorination in methanol produced the same chloro ether products as methyl hypochlorite as well as relatively small amounts of dichlorides.

In considering the mechanistic implications of our results we were particularly interested in accounting for the role of the solvent methanol in promoting the ionic electrophilic addition of methyl hypochlorite. It seems to us that the inertness of methyl hypochlorite⁶ toward alkenes in

typical aprotic, nonnucleophilic solvents used for bromination and chlorination (i.e., CCl₄, CH₂Cl₂, hydrocarbons) could be due to the inability of methyl hypochlorite and an alkene to form an ion-pair intermediate (27). This could be



related to the high basicity (and hence instability) of the methoxide ion. Scheme I presents two possible mechanisms which could account for the role of methanol and, therefore, circumvent the problem of the formation of the high-energy ion pair (27). Addition to the 1,3-pentadiene system is used as an example. Scheme I suggests that the diene reacts with hypochlorite in a fast, readily reversible step to produce charge-transfer (or π) complexes, 28 and 29. Two mechanisms are then possible.⁷ In mechanism i (ionization), a rate-determining ionization of the π complex occurs to yield the ion-pair intermediates, 30 and 31. In this mechanism methanol is assigned the specific role of promoting ionization of the π complex by stabilizing the methoxide ion via hydrogen bonding.⁸ Reaction of 30 and 31 with the nucleophiles methanol or methoxide ion takes place in a

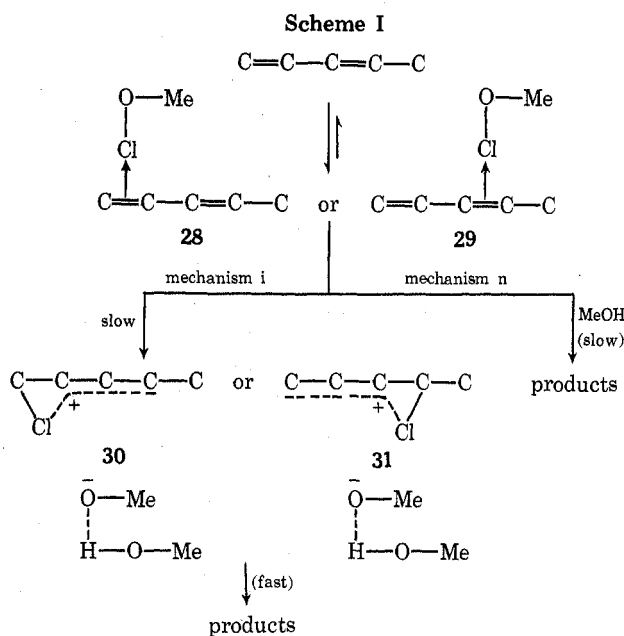


Table I
Reaction of Dienes with Methyl Hypochlorite and Chlorine

Reactants	Yield, %	Products, % ^a						
		4a,b ^b	5	6a,b ^b	7	11	12a,b ^b	Dichlorides
3a, MeOCl, MeOH	85	14	4	37	45			
3a, Cl ₂ , MeOH	70	27	7	22	29			14.5 ^c
3b, MeOCl, MeOH	88	1.3	0.2	43	55			
3b, Cl ₂ , MeOH	62	6	1.5	28	45			20 ^c
3a, MeOCl (radical)	84		37		44	2.5	15.5	
3b, MeOCl (radical)	96		30		54	4	12	
Reactants		13	14 ^d		19 ^d	18	20	Dichlorides
2, MeOCl, MeOH ^{e,f}	98	61	25					
2, Cl ₂ , MeOH ^{e-g}	70	59	18					14 ^c
2, MeOCl (radical) ^e	98		9		80.5	4	3.5	
Reactants		22	23			26		Dichlorides
1, MeOCl, MeOH	85	70	30					
1, Cl ₂ , MeOH	76	60.5	26					13.5 ^c
1, MeOCl (radical)	86		86			14		

^a The product percentages are normalized to 100%. ^b The products formed are, from 3a, *threo*-4-chloro-3-methoxypentene (4a), *cis*-5-chloro-4-methoxy-2-pentene (6a), *cis*-4-chloro-5-methoxy-2-pentene (12a), and from 3b, *erythro*-4-chloro-3-methoxypentene (4b), *trans*-5-chloro-4-methoxy-2-pentene (6b), and *trans*-4-chloro-5-methoxy-2-pentene (12b). ^c In the reactions with Cl₂ the following dichloride products are also formed: from 3a, 3,4-dichloropentene (8) (4.5%), 4,5-dichloro-2-pentene (9) (5%), 1,4-dichloro-*trans*-2-pentene (10) (5%); from 3b, 8 (3%), 9 (11%), 10 (6%); from 2, 3,4-dichloro-3-methylbutene (16) (6%) and 1,4-dichloro-2-methyl-*trans*-2-butene (17) (8%); from 1, 3,4-dichlorobutene (24) (7%) and 1,4-dichloro-*trans*-2-butene (25) (6.5%). ^d Compounds 14 and 19 are assigned the *trans* (*E*) configuration.^{3,5} ^e 2-Chloromethyl-1,3-butadiene (15) was obtained in the reactions of 2: with MeOCl, MeOH, 14%; with Cl₂, MeOH, 8%; with MeOCl, radical, 3%. ^f A minor VPC peak of short retention time was observed (probably 1-chloro-2-methyl-1,3-butadiene, since this compound is reported^{4b} in the chlorination of 2). ^g A compound, assigned the structure *cis*-1-chloro-2-methyl-4-methoxy-2-butene (21), was obtained in a quantity equal to 1.5% in this reaction.

fast step. In mechanism n (nucleophilic), the role of the methanol is to make a rate-determining nucleophilic attack on the π complexes 28 and 29.⁹ Considering the fact that chlorinations of alkenes¹⁰ occur rapidly in aprotic nonnucleophilic solvents by mechanism i, it would seem highly unlikely that chlorinations in methanol would proceed by mechanism n where attack by methanol is rate determining. A sensitive test for similarity of reaction mechanisms between the two electrophiles is that if mechanism i is operative, then essentially identical intermediate cations (30 and 31) should be obtained. Therefore, the ratio of 1,2 to 1,4 methoxy chlorides obtained from electrophilic attack on a particular double bond of a diene should then be very similar for chlorine and methyl hypochlorite.

Analysis of the data on the ionic reactions (Table I) shows that product ratios from chlorine and methyl hypochlorite are strikingly similar. These are compared in Table II in terms of relative reactivities of double bonds and as the ratio of 1,2 to 1,4 products resulting from attack by chlorine at a particular carbon atom. In examining the data on relative reactivities of the double bonds in the unsymmetrical dienes, it is seen that in reaction with isoprene the only products detected result from attack at the methyl-substituted 1,2 bond.¹¹ The relative reactivities of the double bonds in the 1,3-pentadienes (3a,b) are shown in Table II. In each reaction the nonsubstituted (1,2) bond in 3a,b is attacked to a greater extent than the methyl-substituted

Table II
Bond Reactivities and Ratios of 1,2 and 1,4 Adducts

Reactants	Reactivities of bonds in 3a and 3b (1,2/3,4)	Ratio ^e of chloromethoxy products (1,2 adduct/1,4 adduct)	
		From attack on 1,2 bond	From attack on 3,4 bond
3a, MeOCl	4.6 ^a	0.82	3.5
3a, Cl ₂	1.45 ^b	0.76	3.9
3b, MeOCl	65 ^c	0.96	6.5
3b, Cl ₂	8.0 ^d	0.62	4.0
1, MeOCl		2.3	
1, Cl ₂		2.3	
2, MeOCl		2.4	
2, Cl ₂		3.2	

^a (6a + 7)/(4a + 5). ^b (6a + 7 + 9)/(4a + 5 + 8). ^c (6b + 7)/(4b + 5). ^d (6b + 7 + 9)/(4b + 5 + 8). ^e E.g., for 3a (MeOCl), attack on 1,2 bond, 6a/7 = 0.82.

(3,4) bond. A clear difference between chlorine and methyl hypochlorite is also evident from this data.¹² The relative rates of attack at the 1,2 vs. the 3,4 bond in 3a and 3b is appreciably greater for methyl hypochlorite than for chlorine (4.6 vs. 1.5 for 3a and 65 vs. 8 for 3b).

The data on bond reactivities of the dienes would seem to be most easily explained by assuming that both reactions with chlorine and methyl hypochlorite proceed by

ionization mechanisms (mechanism i, Scheme I) in which appreciable carbonium ion character has developed in the transition state preceding the ion pair (30, 31).¹³ Therefore the relative reactivities of the double bonds toward these electrophiles are a reflection of the stabilities of the allylic carbonium ions in ion pairs 30 and 31. For example, the two possible allylic carbonium ions in ion pairs 30 and 31 from 1,3-pentadiene are shown in Scheme I. It is seen that the carbonium ion arising from bonding of chlorine to C₁ is a resonance hybrid of two contributing secondary ions but that bonding at C₄ gives a hybrid of a secondary and a primary ion. The fact that methyl hypochlorite gives an even larger percentage of attack at the 1,2 bond in 3a and 3b than does chlorine may be explained by taking into account that chlorine is far more reactive than methyl hypochlorite.¹⁴ Greater reactivity implies that the transition state preceding intermediates (30 and 31) for ionization of the π complex (28, 29) in chlorination would be attained "earlier"—before as much carbonium ion character has developed—than would be true for the reaction with methyl hypochlorite.

Additional evidence that both methyl hypochlorite and chlorine react by similar carbonium ion mechanisms is obtained by comparing the relative amounts of 1,2 and 1,4 chloromethoxy product obtained from each of the dienes. These data are summarized in Table II. These data show that attack on a particular bond in any one of the dienes by either chlorine or methyl hypochlorite yields similar ratios of chloromethoxy products. The obvious explanation is that both chlorine and methyl hypochlorite yield essentially identical cationic intermediates which give products by reaction with methanol. The site of attack in the ionic intermediates by methanol apparently corresponds to the positions where the positive charge is most stable. That is, in the ionic intermediates which would be obtained from attack on dienes 1, 2, and 3a,b (3,4 bond, intermediate 31), where the 1,4 adduct would arise from attack by methanol at a primary carbon, the main product is the 1,2 adduct (1,2/1,4 ratios vary from 2.3 to 6.5). In the case where the 1,4 adduct is obtained by attack by methanol on a secondary carbon atom (initial attack on the 1,2 bond in 3a,b, intermediate 30) it is formed in larger amount than the 1,2 adduct (1,2/1,4, 0.62–0.96).

Turning attention to the principal aim of our investigation which concerns bond reactivities in unsymmetrical dienes, the data presented above seem to indicate that reactivities of the bonds in a diene toward an electrophile can be predicted on the basis of the carbonium ion stability of the intermediates. This conclusion differs from that which Poutsma¹⁰ developed from extensive studies on the reactivities of monoalkenes (mostly acyclic, aliphatic) toward chlorine in aprotic solvents. He found that alkene reactivity toward chlorine depends upon the basicity or nucleophilicity of the π bond rather than upon the stability of the expected carbonium ion; the basicity of the alkene is related to the degree of alkyl substitution on the double bond. For example, the nearly equivalent reactivity of 2-butene and isobutylene is explained by assuming that the transition state for reaction of chlorine with these alkenes is reactant-like rather than intermediate-like, so that the potential for greater carbonium ion stabilization with isobutylene (tertiary vs. secondary) is not evident in the transition state.

Concerning the dienes included in the study, isoprene (2) would be expected to show greater reactivity at the 1,2 bond both on the basis of alkene basicity and carbonium ion stability, but in the case of the 1,3-pentadienes (3a,b) there is not a clear choice. For example, Poutsma's data on

chlorination shows the relative reactivities of 1-butene, *cis*-2-butene, and *trans*-2-butene to be 1:63:50, respectively. On this basis we might expect the relative reactivities of the double bonds in the 1,3-pentadienes to be 1:63:50 for reaction at the 1,2, the *cis* 3,4, and the *trans* 3,4 bonds, respectively. In fact we find the relative reactivities to be 1:0.22:0.015 for reaction with methyl hypochlorite and 1:0.69:0.12 for reaction with chlorine.¹⁵ Clearly, the effect of methyl substitution in the 1,3-pentadiene system is quite the contrary to what would be predicted on the basis of the monoalkenes. Reactivity is found to be much greater at the nonsubstituted bond. As we have stated above, the relative reactivities of the bonds in 3a,b seem to be best interpreted from the viewpoint that the transition state for chlorination of conjugated dienes is quite different from that for monoalkenes, and is one in which significant carbonium ion character is developed. Another point of interest is that the substituted (3,4) bond (3a,b) in the *cis* diene is much more reactive than in the *trans* diene.¹⁵

Finally, we would like to comment briefly on the radical addition of methyl hypochlorite to the dienes. A common characteristic of the radical reactions is that the 1,4 adduct is produced in much larger amounts than in the ionic additions. In additions to the unsymmetrical dienes the relative bond reactivities are appreciably different than for ionic reactions. The 1,3-pentadienes exhibit far more attack at the methyl-substituted (3,4) bond than is noted in ionic addition; e.g., for ionic additions of methyl hypochlorite to 3a and 3b, the 1,2:3,4 bond reactivities (Table II) are 4.6 and 65, respectively, whereas, the relative reactivities in radical addition are 1.13 and 0.72 for addition to 3a and 3b, respectively. The radical reaction of methyl hypochlorite with isoprene (2) shows less discrimination than the ionic reaction, in that appreciable attack (12%) at the 3,4 bond is observed in the radical reaction.

Experimental Section

General. Dienes and solvents were obtained commercially in high purity. Methyl hypochlorite was prepared as a solution in methylene chloride by a modification of the method used by Jenner to prepare *n*-butyl hypochlorite.¹⁶ NMR spectra were obtained on a Varian T-60A spectrometer and ir spectra on Beckman IR-10 or Perkin-Elmer 337 spectrophotometers. VPC analysis of products from 1 and 3a,b was done on a Hewlett-Packard 5750 flame ionization chromatograph and from 2 on an Aerograph 90 P-3 thermal conductivity instrument.

Reaction Conditions. Ionic reactions were done at 0–2°C in methanol which had been previously saturated with oxygen gas. The diene was present in 0.02 mol fraction with respect to the methanol. Methyl hypochlorite and chlorine were added as ca. 1 M solutions (in methylene chloride and carbon tetrachloride, respectively) in amounts sufficient to consume 25% of the diene. Reactions of 2 and 3a,b with methyl hypochlorite required about 1 h for completion. The reaction of 1 with methyl hypochlorite was much slower (30% complete, 1 h; 80% complete, 18 h). After completion, reaction mixtures were poured into ice water and the products isolated by extraction with pentane.

Experiments were done which showed that the dichlorides and methoxy chlorides formed in the above reactions did not react with solvent under the conditions used. For example, a mixture of the dichlorides from 2 (16 and 17) was allowed to stand in methanol for 1 h at 0°C and then poured into ice water and extracted into pentane. The ratio of dichlorides was unchanged and methoxy chlorides were not formed. The same experiment performed with the dichlorides of 3a (8, 9, 10) and with the methoxy chlorides of 3a (6a and 7) showed that these compounds were likewise unaffected by the reaction conditions.¹⁷

Radical reactions were done as follows: methyl hypochlorite (ca. 1 M solution in methylene chloride) sufficient to consume 10% of the diene was added to the diene (0.5 mol fraction in CCl₄) at 0–5°C (–5 to –10°C for 1). Reactions had a tendency to show induction periods and to proceed exothermically with dienes 2 and 3a,b and were completed when addition of hypochlorite was fin-

ished. With 1 the reaction was considerably slower (50% complete, 30 min) so sun-lamp irradiation was employed to hasten the reaction.

Analysis Procedures. Mixtures of products were analyzed by VPC with the following columns: column A, 2.5% β,β -oxydipropionitrile, on 80-100 Chromosorb W (AW-DMCS), 4 ft \times 0.25 in. SS; column B, 2.5% SE-30 on 80-100 Chromosorb W (AW-DMCS). VPC analysis is based on ratios of normalized peak areas. Peak areas were normalized by obtaining VPC response factors for each of the isolated compounds. This was done by analysis of standard mixtures of the pure compounds with an internal standard (the same internal standards were used to obtain yields in reactions).

Identification of Isomers. Assignment of structures to the compounds reported below is based on interpretation of NMR and ir spectra and on certain rearrangement experiments. Most of the isomers are readily distinguished by NMR and ir because of differences such as the number or location of vinyl hydrogens but certain of the isomers differ only in the positions of chlorine atoms and methoxyl groups. Such pairs of isomers are the following: 5,7; 6a,b, 12a,b; 13,18; 14,19; 22,26. Structural distinctions between these isomers were made on the following basis.

(1) On the assumption that the reactions in methanol, Cl_2 , and CH_3OCl are ionic and that the reaction of methyl hypochlorite at high diene concentration is radical, it would be expected that Markownikoff adducts would result from the former (6a,b, 13, and 22) and non-Markownikoff adducts from the latter (12a,b, 18, and 26), since in the former reactions chlorine would be the electrophile and in the latter reaction the methoxyl radical would be the chain carrier. It is also reasonable that the 1,4 adduct resulting from ionic addition to 2 should be 14 rather than 19 since the only 1,2 adduct observed is 13 (resulting from attack at the 3,4 bond). It is not unexpected that radical addition to 2 should occur primarily via attack by the methoxyl radical on the 3,4 bond and therefore result in 19. A similar argument could be made for the structure of the principal 1,4 adduct from 3b under ionic conditions. Since the overwhelming 1,2 adduct (6a) results from attack at the 1,2 bond, it is highly unlikely that the major 1,4 adduct would result from attack at the 3,4 bond (thus forming 5).

(2) It is known that methine protons bonded to carbons bearing chlorine exhibit larger downfield chemical shifts than protons bonded to carbons bearing methoxyl groups.⁵ The pairs of isomers assigned structures 5,7 and 22,26 exhibited chemical shifts for methine hydrogens in accordance with this principle, i.e., 5, δ 4.5, and 7, 3.7; 22, 3.72, and 26, 4.35. Compound 20 exhibited the methine absorption at δ 4.38, in close agreement with that in 26.

(3) Observations on rearrangement of isomers provided additional evidence for structural assignments. Solutions of 13, 18, and 20 in carbon tetrachloride to which anhydrous zinc chloride had been added were kept at 50° for several hours and analyzed at various times by NMR. Compound 18 had rearranged about 80% after 2 h to mainly the 1,4-methoxy chloride, 19. After 18 h 20 had rearranged about 60% to mainly 14 and some 21 but in the same time 13 was essentially unchanged. The allylic chlorides 18 and 20 would be expected to rearrange to the 1,4-methoxy chlorides 19 and 14, respectively, whereas 13, in which the chlorine is not allylic, should be much more stable. When a mixture of mainly 7 and 12 in carbon tetrachloride was treated with anhydrous zinc chloride and allowed to stand at room temperature for 2 h, 12 rearranged to 5 (observed by NMR). It was also observed that when separations of mixtures containing 5, 7, and 12 were attempted by large scale preparative VPC, samples of either 5 or 12 always contained both isomers. For example, 5 could be obtained free of 7 (and pure samples of 7 were readily obtained) but always contained appreciable 12 despite the order of retention times, $12 < 7 < 5$. Isomers 5 and 12 can be interconverted by allylic rearrangement of the chloride.

Products from Butadiene (1). Products from 1 were analyzed on VPC columns A and B. On column A (50°), retention times (min) follow: 24, 2.2; 22, 2.2; 26, 2.7; 23, 8.2; 25, 12.6. On column B (35°, 11 ft \times 0.125 in.): 24, 4.5; 22 and 26, 5.0. Dichlorides 24 and 25 are known compounds.^{4a} Methoxy chlorides were isolated from large-scale reactions by distillation and preparative VPC.

Summary of NMR spectra (parts per million downfield from Me_4Si , CCl_4): 22, 3.25 (s, 3, CH_3O), 3.42 (m, 2, CH_2), 3.72 (m, 1, CHOCH_3), 5.08-5.49 (m, 2, $\text{CH}_2=\text{CH}$), 5.79 (m, 1, $\text{CH}_2=\text{CH}$); 23, 3.26 (s, 3, CH_3O), 3.76-4.10 (m, 4, CH_2Cl and CH_2OCH_3), 5.69-5.90 (m, 2, $\text{CH}=\text{CH}$); 26, 3.34 (s, 3, CH_3O), 3.47 (m, 2, CH_2), 4.35 (m, 1, CHCl), 5.04-5.50 (m, 2, $\text{CH}_2=\text{CH}$), 5.90 (ddd, 1, $\text{CH}_2=\text{CH}$, $J = 9.4$, $J' = 6.9$, $J'' = 16.0$ Hz).

Infrared absorptions (cm^{-1} , CCl_4): 22, 3085 ($\text{C}=\text{CH}$), 2830 (CH_3O), 1640 ($\text{C}=\text{C}$), 1116 (CH_3O), 989 and 934 ($\text{CH}=\text{CH}_2$ bending); 23, 3020 ($\text{C}=\text{CH}$), 2830 (CH_3O), 1120 (CH_3O), 965 (trans $\text{CH}=\text{CH}$); 26, 3090 ($\text{C}=\text{CH}$), 2830 (CH_3O), 1645 ($\text{C}=\text{C}$), 1126 (CH_3O), 984 and 930 ($\text{CH}=\text{CH}_2$ bending).

Products from Isoprene (2). Products from 2 were analyzed by VPC on column A (60°), which gave the following retention times (min): 15, 2.2; 18, 3.0; 16, 3.5; 13, 4.8; 20, 5.3; 21, 10.9; 19, 12.7; 14, 15.0; and 17, 20.7. All of the products from 2 were isolated by distillation of large-scale preparations followed by preparative VPC (the most generally useful column was 5% Silicone DC-550 on 80-100 Chromosorb W, AW-DMCS, 6 ft \times 0.37 in., glass). Dichlorides 16 and 17 and the monochloride 15 have been previously identified.^{4b}

NMR spectra (CCl_4): 13, 1.31 (s, 3, CH_3), 3.15 (s, 3, CH_3O), 3.38 (s, 2, CH_2), 5.00-5.40 (m, 2, $\text{CH}_2=\text{CH}$), 5.53-6.04 (m, 1, $\text{CH}_2=\text{CH}$); 14, 1.75 (d, 3, CH_3 , $J = 1.0$ Hz), 3.24 (s, 3, CH_3O), 3.88 (d, 2, CH_2OCH_3 , $J_{34} = 6.0$ Hz), 3.93 (s, 2, CH_2Cl), 5.62 (dt, 1, $\text{CH}=\text{C}$, $J_{34} = 6.0$, $J = 1.0$ Hz); 18, 1.62 (s, 3, CH_3), 3.37 (s, 3, CH_3O), 3.43 (s, 2, CH_2), 5.08 [dd, 1, cis $\text{CH}=\text{C}(\text{H})\text{H}$, $J = 9.8$, $J' = 1.3$ Hz], 5.27 [dd, 1, trans $\text{CH}=\text{C}(\text{H})\text{H}$, $J = 16.4$, $J' = 1.3$ Hz], 6.00 (dd, 1, $\text{CH}=\text{CH}_2$, $J = 16.4$, $J' = 9.8$ Hz); 19, 1.72 (s, 3, CH_3), 3.25 (s, 3, CH_3O), 3.77 (s, 2, CH_2OCH_3), 4.05 (d, 2, CH_2Cl , $J_{34} = 7.2$ Hz), 5.65 (t, 1, $\text{CH}=\text{C}$, $J_{34} = 7.2$ Hz); 20, 1.80 (dd, 3, CH_3 , $J = 1.4$, $J' = 0.8$ Hz), 3.33 (s, 3, CH_3O), 3.53 (m, 2, CH_2OCH_3), 4.38 (t, 1, CHCl , $J_{34} = 6.8$ Hz), 4.90 [q, 1, $\text{C}=\text{C}(\text{H})\text{H}$, $J = 1.4$ Hz], 5.03 [q, 1, $\text{C}=\text{C}(\text{H})\text{H}$, $J = 0.8$ Hz]; 21, 1.87 (dd, 3, CH_3 , $J = 1.6$ Hz), 3.27 (s, 3, CH_3O), 3.93 (d, 2, CH_2OCH_3 , $J_{34} = 6.8$ Hz), 4.03 (s, 2, CH_2Cl), 5.48 (dt, 1, $\text{CH}=\text{C}$, $J_{34} = 6.8$, $J = 1.6$ Hz).

Infrared spectra (CCl_4): 13, 3085 ($\text{C}=\text{CH}$), 2830 (CH_3O), 1640 ($\text{C}=\text{C}$), 1106 (ether), 995, 931 ($\text{CH}=\text{CH}_2$ bending); 14, 2825 (CH_3O), 1120 (ether); 18, 3080 ($\text{C}=\text{CH}$), 2820 (CH_3O), 1112 (ether), 988, 926 ($\text{CH}=\text{CH}_2$ bending); 19, 2820 (CH_3O), 1660 ($\text{C}=\text{C}$), 1112 (ether); 20, 3080 ($\text{C}=\text{CH}$), 2820 (CH_3O), 1128 (ether), 909 ($\text{C}=\text{CH}_2$ bending); 21, 2825 (CH_3O), 1105 (ether).

Products from the 1,3-Pentadienes (3a,b). Products from 3a,b were analyzed by VPC on columns A and B. On column A (60°) retention times (min) follow: 4a and 4b, 1.5; 8, 2.0; 6b, 2.9; 6a, 3.3; 9, 3.3; 7, 4.2; 12a and 12b, 4.2; 5, 6.2; 10, 8.3. On column B (18 ft, 70°): 9, 8.2; 6a, 8.9; on column B (6 ft, 32°), 11, 8.0; 12a, 12.8; 12b, 14.0; 7, 14.8. Dichlorides 8, 9, and 10 were identified previously.¹⁸ Except for compounds 12a and 12b, identifications were made on pure samples of the isolated compounds obtained by preparative VPC. Columns used for preparative VPC were 5% DEGS, 15 ft \times 0.5 in., steel and 5% Silicone DC-550, 6 ft \times 0.37 in., glass.

Pure samples of 12 were not obtained because of the similar VPC retention time to 7 and because some rearrangement of 12 to 5 always occurred under the conditions used for preparative VPC collection. Identification of 12 was made on mixtures of 12 with 5 and 7. Identification is based on the rearrangement observations described above and on the following NMR observations. Methoxyl and methyl absorptions for 12 occur separately from those for 5 and 7. Decoupling experiments on the mixtures of 12 (with 5 and 7) showed that irradiation at δ 5.7 caused decoupling of the methyl doublet of 12, confirming that the methyl group was bonded to the vinyl group. Decoupling of the methyl doublets of 5 and 7 was accomplished by irradiation of their methine regions (δ 4.5 and 3.7, respectively). Isomers 4a and 4b were isolated from ionic reactions of 3a and 3b, respectively, and were found to be uncontaminated with each other. Assignment of the threo structure to 4a and the erythro structure to 4b is made on the assumption that the stereospecific addition of chlorine and methoxyl would be anti. Compound 11 was isolated from the reaction of 3b with methyl hypochlorite. It apparently contained comparable amounts of the erythro and threo isomers which are responsible for the two methyl doublets (NMR).

NMR spectra (CCl_4): 4a, 1.38 (d, 3, CH_3 , $J_{45} = 6.4$ Hz), 3.28 (s, 3, CH_3O), 3.58 (dd, 1, CHOCH_3 , $J_{34} = 5.0$, $J_{23} = 5.0$ Hz), 3.95 (dq, 1, CHCl , $J_{45} = 6.4$, $J_{34} = 5.0$ Hz), 5.03-5.43 (m, 2, $\text{CH}=\text{CH}_2$), 5.52-6.10 (m, 1, $\text{CH}=\text{CH}_2$); 4b, 1.45 (d, 3, CH_3 , $J_{45} = 6.5$ Hz), 3.28 (s, 3, CH_3O), 3.50 (dd, 1, CHOCH_3 , $J_{34} = 5.3$, $J_{23} = 5.3$ Hz), 3.85 (dq, 1, CHCl , $J_{45} = 6.5$, $J_{34} = 5.3$ Hz), 4.93-5.40 (m, 2, $\text{CH}=\text{CH}_2$), 5.50-6.07 (m, 1, $\text{CH}=\text{CH}_2$); 5, 1.58 (d, 3, CH_3 , $J_{45} = 6.8$ Hz), 3.25 (s, 3, CH_3O), 3.78-3.95 (m, 2, CH_2), 4.22-4.72 (m, 1, CHCl), 5.45-5.88 (m, 2, $\text{CH}=\text{CH}$); 6a, 1.72 (dd, 3, CH_3 , $J_{12} = 7.0$, $J_{13} = 1.5$ Hz), 3.23 (s, 3, CH_3O), 3.23 [dd, 1, $\text{C}(\text{H})\text{H}$, $J_{55'} = 10.5$, $J_{45} = 6.2$ Hz], 3.47 [dd, 1, $\text{C}(\text{H})\text{H}$, $J_{55'} = 10.5$, $J_{45'} = 6.2$ Hz], 4.07 (ddd, 1, CHOCH_3 , $J_{34} = 8.5$, $J_{45} = 6.2$, $J_{45'} = 6.2$ Hz), 5.15 (q of dd, 1, $\text{CH}_3\text{CH}=\text{CH}$, $J_{23} = 11.0$, $J_{34} = 8.5$, $J_{13} = 1.5$ Hz), 5.73 (dq, 1,

$\text{CH}_3\text{CH}=\text{CH}$, $J_{23} = 11.0$, $J_{12} = 7.0$ Hz); **6b**, 1.75 (dd, 3, CH_3 , $J_{12} = 6.2$, $J_{13} = 1.2$ Hz), 3.27 (s, 3, CH_3O), 3.30 [dd, 1, $\text{CH}(\text{H})$, $J_{55'} = 11.0$, $J_{54} = 6.0$ Hz], 3.44 [dd, 1, $\text{CH}(\text{H})$, $J_{55'} = 11.0$, $J_{54} = 6.0$ Hz], 3.61 (ddd, 1, CHOCH_3 , $J_{34} = 7.2$, $J_{45} = 6.0$, $J_{45'} = 6.0$ Hz), 5.30 (ddd, 1, $\text{CH}_3\text{CH}=\text{CH}$, $J_{23} = 15.5$, $J_{34} = 7.2$, $J_{13} = 1.2$ Hz), 5.75 (dq, 1, $\text{CH}_3\text{CH}=\text{CH}$, $J_{23} = 15.5$, $J_{12} = 6.2$ Hz); **7**, 1.18 (d, 3, CH_3 , $J_{45} = 6.6$ Hz), 3.18 (s, 3, CH_3O), 3.43–3.90 (m, 1, CHCl), 3.90–4.07 (m, 2, CH_2), 5.53–5.77 (m, 2, $\text{CH}=\text{CH}$); **11**, 1.15 (d, CH_3 , $J_{45} = 6.0$ Hz), 1.18 (d, CH_3 , $J_{45} = 6.2$ Hz), 3.37 (s, 3, CH_3O), 3.20–3.60 (m, 1, CHOCH_3), 4.07–4.50 (m, 1, CHCl), 5.07–5.50 (m, 2, $\text{CH}=\text{CH}_2$), 5.63–6.32 (m, 1, $\text{CH}=\text{CH}_2$); **12a**, 1.73 (d, CH_3 , $J_{12} = 5.0$ Hz), 3.33 (s, CH_3O); **12b**, 1.75 (d, CH_3 , $J_{12} = 5.2$ Hz), 3.32 (s, CH_3O).

Infrared spectra (cm^{-1}): **4a** (liquid film), 3070 ($\text{C}=\text{CH}$), 2810 (CH_3O), 1075 (ether), 920 and 980 ($\text{CH}=\text{CH}_2$ bending); **4b** (CCl_4), 3080 ($\text{C}=\text{CH}$), 2825 (CH_3O), 1640 ($\text{C}=\text{C}$), 1095 (ether), 933 and 999 ($\text{CH}=\text{CH}_2$ bending); **5** (liquid film), 2820 (CH_3O), 1120 (ether), 960 (trans $\text{CH}=\text{CH}$); **6a** (liquid film), 2825 (CH_3O), 1655 ($\text{C}=\text{C}$), 1100 (ether), 750 (cis $\text{CH}=\text{CH}$ bending); **6b** (liquid film), 2825 (CH_3O), 1095 and 1110 (ether), 965 (trans $\text{CH}=\text{CH}$ bending); **7** (liquid film), 2820 (CH_3O), 1113 and 1090 (ether), 966 (trans $\text{CH}=\text{CH}$ bending); **11** (CCl_4), 3080 ($\text{C}=\text{CH}$), 2825 (CH_3O), 1100 (ether), 986 and 928 ($\text{CH}=\text{CH}_2$ bending).

Acknowledgement. Support for this work was provided by the Research Corporation and by the donors of the Petroleum Research Fund, administered by the American Chemical Society.

Registry No.—1, 106-99-0; 2, 78-79-5; **3a**, 1574-41-0; **3b**, 2004-70-8; **4a**, 57512-99-9; **4b**, 57513-00-5; 5, 57513-01-6; **6a**, 57513-02-7; **6b**, 57513-03-8; **7**, 57513-04-9; *erythro*-11, 57513-05-0; *threo*-11, 57513-06-1; **12a**, 57513-07-2; **12b**, 57513-08-3; **13**, 57513-09-4; **14**, 57513-10-7; **18**, 57513-11-8; **19**, 57513-12-9; **20**, 6986-42-1; **21**, 57513-13-0; **22**, 7795-90-6; **23**, 57513-14-1; **26**, 57513-15-2; methyl hypochlorite, 593-78-2; chlorine, 7782-50-5.

References and Notes

- (1) E. g., see W. A. Pryor, "Free Radicals", McGraw-Hill, New York, N.Y., 1966, pp 120, 167.
- (2) W. Oroshnik and R. A. Mallory [*J. Am. Chem. Soc.*, **72**, 4608(1950)] have studied reactions of isoprene with *tert*-butyl hypochlorite; C. Walling and R. T. Clark [*J. Org. Chem.*, **39**, 1962 (1974)] report the reaction of *tert*-butyl hypochlorite with alkenes in alcohol, catalyzed by boron trifluoride.
- (3) The trans (*E*) structure is assigned to **14** and **19** and the cis structure to **21** on the following basis. (1) Electrophilic additions to dienes (radical and ionic) are known to yield predominantly trans rather than cis 1,4 adducts (e.g., chlorination of butadiene^{4a} and isoprene^{4b}). (2) the NMR absorptions due to the methyl groups in **14**, **19**, and **21** are consistent with the general finding⁵ that cis allylic methyl groups exhibit higher field absorptions (δ 1.75 for **14** vs. 1.87 for **21**) and larger allylic coupling constants (**14**, 1.0 Hz; **21**, 1.6 Hz; **19**, < 0.5 Hz) than do corresponding trans methyls.
- (4) (a) M. L. Poutsma, *J. Org. Chem.*, **31**, 4167 (1966); (b) G. D. Jones, N. B. Tefertiller, C. F. Raley, and J. R. Runyon, *ibid.*, **33**, 2946 (1968).
- (5) E.g., L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry", 2nd ed, Pergamon Press, Elmsford, N.Y., 1969, pp 164, 225, and 316.
- (6) We have completed a study on the reaction of methyl hypochlorite with styrene in the aprotic solvents, nitrobenzene and acetonitrile. A manuscript describing the results of this study will be submitted to this journal in the near future.
- (7) Mechanism i and mechanism n would be examples of two classes of electrophilic addition mechanisms designated AdeC_1 and AdeC_2 , respectively; e.g., see F. Garnier and J. Dubois, *Bull. Soc. Chim. Fr.*, 3797 (1968).
- (8) In a recent report [*J. Am. Chem. Soc.*, **97**, 1977 (1975)] J. E. DuBois and M. F. Ruasse have concluded from kinetic evidence that the bromination of alkenes in protic, nucleophilic solvents involves no nucleophilic contribution by the solvent in the transition state and that these solvents effect the rate by stabilization of the bromide ion.
- (9) Mechanisms in which the rate-determining step is a nucleophilic attack have recently been proposed for some electrophilic addition reactions, e.g., bromination by Br_3^- [J. E. Dubois and X. Q. Huynh, *Tetrahedron Lett.*, 3369 (1971)] and certain electrophilic additions to 3-*tert*-butylcyclohexene [G. Bellucci, G. Ingrassio, R. Marioni, E. Mastrarilli, and I. Marcelli, *J. Org. Chem.*, **39**, 2562 (1974)].
- (10) E.g., see M. L. Poutsma, *J. Am. Chem. Soc.*, **87**, 4285 (1965).
- (11) It is unlikely that significant amounts of products resulting from attack at the 3,4 bond in **2** were overlooked. All peaks appearing in the VPC of the ionic reaction products were collected and examined carefully by NMR. No evidence for the presence of 4-chloro-3-methoxy-2-methylbutene could be found. A VPC peak with the retention time of the 1,4 adduct (**19**) was observed in the product from chlorination of **2** (in methanol) in a quantity equal to ca. 0.5% of the total product.
- (12) It is conceivable that methyl hypochlorite could react in methanol via decomposition to chlorine. The fact that methyl hypochlorite exhibits different relative reactivities toward the double bonds than chlorine does, as well as the fact that significant quantities of dichlorides are not obtained with methyl hypochlorite, is evidence that decomposition to chlorine does not occur.
- (13) A reviewer has suggested that regioselectivity in addition to these dienes may be governed by relative stabilities (and hence concentrations) of the π complexes, i.e., **28** and **29**. Although this could well be a factor in determining relative reactivities of the double bonds, we do not see how the importance of this factor could be determined separately from that of the rate-determining ionization step.
- (14) Although we have no quantitative data on the comparison between the rates of reaction of chlorine and methyl hypochlorite, qualitative observations (see Experimental Section) indicate that they probably differ in rate by several orders of magnitude.
- (15) We do not mean to imply that the 1,2 double bonds in **3a** and **3b** are of equal reactivity. There are little data available on the relative reactivities of conjugated dienes among themselves or in comparison to nonconjugated alkenes. We hope to explore this problem in the near future.
- (16) E. L. Jenner, *J. Org. Chem.*, **27**, 1031 (1962).
- (17) The dichlorides (particularly **17** and **10** with two allylic halogens) would be expected to solvolyze at rates comparable to the most reactive of the methoxy chlorides, i.e., those containing allylic chloride. Small amounts of solvolysis of the dichlorides would have been detected by the formation of the known methoxy chlorides. The fact that the ratio of **6a** and **7** did not change also confirms stability to solvolysis since **7** is an allylic chloride but **6a** is not.
- (18) A paper describing the chlorination of **3a,b** has been accepted for publication in this journal.